Unusual rearrangement of an N-heterocyclic carbene via a ring-opening and ring-closing process

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Electronic Supplementary Information

General Procedures. All reactions were performed under Ar atmosphere, using standard Schlenk techniques. Column chromatography was performed with silica gel (300-400 mesh). The starting materials 1-(pyridin-2-yl)-1*H*-benzimidazole (**a**)[1] and tosylbis(2-(tosyloxy)ethyl)amine (**b**)[2] were prepared according to the references. All solvents and other chemicals are commercially available.

NMR spectra were measured on a Bruker Avance 400 MHz spectrometer at 298 K. Elemental analyses (C, H, and N) were carried out on a PerkinElmer 240C analytic instrument. Electrospray ionization mass spectra (ESI-MS) were carried out on a LCQ Fleet, Thermo Fisher Scientific mass spectrometer.

Synthesis of c. A mixture of 1-(pyridin-2-yl)-1H-benzimidazole (**a**) (3.90 g, 20.0 mmol) and tosylbis(2-(tosyloxy)ethyl)amine (**b**) (5.67 g, 10.0 mmol) in 150 mL acetonitrile was stirred under Ar atmosphere at 85 ºC for 5 days. The solvent was removed under vacuum, and the residue was washed with ethyl acetate and diethyl ether to give a yellow solid, which was used without further purification.

Synthesis of d. A mixture of 40 ml HBr (48 %), 1.0 g PhOH and compound **c** was stirred at 110 ºC for 24 hours. After cooled to room temperature, the solution was added dropwise into 400 mL acetone and then filtered. The filtered cake was washed with excess acetone until the filtrate turned into colorless to obtain a white solid, which was used without further purification.

Synthesis of $(H_2L)(PF_6)_2$. Coumpound **d** was dissolved in 200 mL water and then the solution of 3.26 g NH_4PF_6 in 100 mL water was added dropwise to give a white precipitate. The precipitate was filtered and washed with excess water,

methanol and diethyl ether to afford a white solid (1.60 g, 2.1 mmol, 21 % yield in total based on tosylbis(2-(tosyloxy)ethyl)amine). ^{1}H NMR (400 MHz, CD_3CN): δ 9.38 (s, 2H), 8.63 (dd, 2H), 8.23-8.17 (m, 2H), 8.12 (td, 2H), 7.90-7.85 (m, 2H), 7.70-7.60 (m, 8H), 4.55 (t, 4H), 3.22 (t, 4H). ^{13}C NMR (100 MHz, CD_3CN): δ 150.44, 147.43, 141.08, 140.88, 132.57, 130.39, 128.56, 128.06, 126.02, 117.51, 116.08, 114.22, 48.29, 47.09. Anal. Calcd for $C_{28}H_{27}N_7F_{12}P_2$: C, 44.75; H, 3.62; N,13.05. Found: C, 44.66; H, 3.65; N,12.99. ESI-MS (*m*/*z*): 606.00 $[M\text{-}PF_6]^+$, 460.25 $[M\text{-}H\text{-}2PF_6]^+$, 230.67 $[M\text{-}2PF_6]^{2+}$.

Synthesis of 1a and 1b.

Route 1: A mixture of $(H_2L)(PF_6)_2$ (75.1 mg, 0.10 mmol) and Ag_2O (69.6 mg, 0.30 mmol) in acetonitrile (3 mL) was stirred in the dark for 12 h at room temperature under Ar atmosphere. Then, the mixture was centrifuged and the solution was stirred with $Ni(PPh_3)_2Cl_2$ (65.6 mg, 0.10 mmol) or $Pd(PPh_3)_2Cl_2$ (70.2 mg, 0.10 mmol) in dark for 12 h at room temperature. After reaction was finished, the mixture was centrifuged. The solution was then treated by excess diethyl ether to afford the crude product, which was dried under vacuum and purified through crystallization of acetonitrile and diethyl ether.

Route 2: 1a: A mixture of $(H_2L)(PF_6)_2$ (225.3 mg, 0.30 mmol), $Ni(OAc)_2{\cdot}4H_2O$ (75.0 mg, 0.30 mmol) in DMSO (10 mL) was stirred under Ar atmosphere at room temperature for 24 h. Then the reaction mixture was centrifuged, and 3 mL dry acetonitrile was added, followed by 80 mL diethyl ether. The precipitate was collected and purified through crystallization of acetonitrile and diethyl ether.

1b: A mixture of $(H_2L)(PF_6)_2$ (75.1 mg, 0.10 mmol), $Pd(OAc)_2$ (22.4 mg, 0.10 mmol) in DMSO (3 mL) was stirred under Ar atmosphere at 80 °C for 12 h. After cooling to room temperature, the reaction mixture was centrifuged, and then 3 mL dry acetonitrile was added, followed by 80 mL diethyl ether. The precipitate was collected and purified through crystallization of acetonitrile and diethyl ether.

1a: yellow solid. Yield: 34 mg, 42 % (route 1); 199 mg, 82 % (88% by NMR, Figure S17) (route 2). ^{1}H NMR (400 MHz, CD_3CN): δ 8.46-8.14 (m, 3H), 8.09 (d, 2H), 7.91 (td, 3H), 7.86-7.79 (m, 2H), 7.69-7.59 (m, 4H), 7.23-6.94 (m, 2H), 5.16-4.91 (m, 1H), 4.80-4.40 (m, 4H), 3.97-3.69 (m, 1H), 3.40-2.90 (m, 3H). ^{13}C NMR (100MHz, CD_3CN): δ 151.89, 150.58, 147.47, 144.49, 141.97, 141.31, 129.03, 128.38, 127.40, 126.96, 126.26, 116.42, 114.61, 113.59, 113.47, 47.56, 46.69, 46.08, 42.39. Anal. Calcd for $C_{28}H_{25}N_7F_{12}P_2Ni$: C, 41.61; H, 3.12; N, 12.13. Found: C, 41.55; H, 3.30; N, 12.41. ESI-MS (*m*/*z*): 516.33 $[M\text{-}H\text{-}2PF_6]^+$, 258.83 $[M\text{-}2PF_6]^{2+}$.

1b: colorless solid. Yield: 42 mg, 49% (route 1); 66 mg, 77 % (91% by NMR, Figure S18) (route 2). ^{1}H NMR (400 MHz, CD_3CN): δ 8.30-8.10 (m, 5H), 8.03-7.83 (m, 5H), 7.74-7.58 (m, 4H), 7.36-7.02 (m, 2H), 5.53-5.40 (m, 1H), 4.98-4.45 (m, 4H), 3.75-3.40 (m, 4H). ^{13}C NMR (100MHz, DMSO-d^6): δ 151.58, 151.04, 142.84, 141.41, 133.89, 132.02, 131.49, 126.42, 126.16, 124.22, 118.57, 117.14, 114.03, 113.14, 53.15, 51.44, 46.62, 46.18. Anal. Calcd for $C_{28}H_{25}N_7F_{12}P_2Pd$: C, 39.29; H, 2.94; N, 11.46. Found: C, 38.92; H, 2.80; N, 11.32. ESI-MS (*m*/*z*): 564.39 $[M\text{-}H\text{-}2PF_6]^+$, 282.83 $[M\text{-}2PF_6]^{2+}$.

Synthesis of 2a.

A mixture of $(H_2L)(PF_6)_2$ (75.1 mg, 0.10 mmol), $Ni(OAc)_2 \cdot 4H_2O$ (25.0 mg, 0.10 mmol) and NaOAc (24.6 mg, 0.30 mmol) in DMSO (3 mL) was stirred under Ar atmosphere at room temperature for 24 h. Then the reaction mixture was centrifuged, and 3 mL dry acetonitrile was added, followed by 80 mL diethyl ether. The precipitate was collected and purified through crystallization of acetonitrile and diethyl ether.

Synthesis of 2b. A mixture of $(H_2L)(PF_6)_2$ (75.1 mg, 0.10 mmol), $Pd(OAc)_2$ (22.4 mg, 0.10 mmol) and NaOAc (24.6 mg, 0.30 mmol) in DMSO (3 mL) was stirred under Ar atmosphere at 80 ^oC for 12 h. After cooling to room temperature, the reaction mixture was centrifuged, and then 3 mL dry acetonitrile was added, followed by 80 mL diethyl ether. The precipitate was collected and purified through crystallization of acetonitrile and diethyl ether.

2a: dark purple solid. Yield: 33 mg, 50 %. ^1H NMR (400 MHz, CD_3CN): δ 8.49 (d, 1H), 8.24-8.15 (m, 1H), 8.09 (d, 2H), 7.95 (d, 1H), 7.72-7.66 (m, 1H), 7.64-7.53 (m, 3H), 7.46 (t, 1H), 7.23 (td, 1H), 7.15-7.00 (m, 3H), 6.79 (d, 1H), 6.34 (td, 1H), 4.82 (t, 1H), 4.54-4.35 (m, 3H), 4.15-4.06 (m,1H), 4.05-3.91 (m, 3H). ^{13}C NMR (100MHz, CD_3CN): δ 183.69, 178.73, 166.21, 151.69, 149.52, 148.75, 143.09, 138.15, 137.24, 137.05, 136.73, 129.90, 126.68, 126.04, 125.40, 124.31, 123.22, 122.35, 112.96, 112.57, 112.45, 110.43, 107.75, 50.24, 48.99, 46.56, 46.49. Anal. Calcd for $C_{28}H_{24}N_7F_6PNi$: C, 50.79; H, 3.65; N,14.81. Found: C, 50.90; H, 3.80; N,15.07. ESI-MS (*m*/*z*): 516.50 $[M\text{-}PF_6]^+$.

2b: red solid. Yield: 38 mg, 54 %. ^1H NMR (400 MHz, CD_3CN): δ 8.78 (d, 1H), 8.28-8.12 (m, 3H), 7.80 (td, 1H), 7.77-7.72 (m,1H), 7.68-7.57 (m, 3H), 7.48 (t, 1H),

7.22 (td, 1H), 7.18 (d, 1H), 7.12 (t, 1H), 7.01 (t,1H), 6.77 (d, 1H), 6.31 (td, 1H), 4.76-4.63 (m, 1H), 4.61-4.40 (m, 3H), 4.26-4.04 (m, 3H), 4.03-3.92 (m, 1H). ^{13}C NMR (100 MHz, CD_3CN): δ 181.61, 176.44, 165.15, 152.45, 151.22, 148.58, 143.56, 140.38, 137.11, 136.11, 135.74, 130.24, 127.02, 126.35, 126.31, 124.96, 123.46, 122.07, 118.57, 113.49, 113.46, 112.96, 110.45, 108.18, 50.95, 49.12, 47.88, 47.84. Anal. Calcd for $C_{28}H_{24}N_7F_6PPd$: C, 47.37; H, 3.41; N, 13.81. Found: C, 47.10; H, 3.27; N, 13.69. ESI-MS (*m*/*z*): 564.50 $[M\text{-}PF_6]^+$.

Conversion from 1a/1b into 2a/2b.

Route 1 with weak base: A mixture of **1a** (80.8 mg, 0.10 mmol) or **1b** (85.6 mg, 0.10 mmol) and NaOAc (24.6 mg, 0.30 mmol) in 3 mL DMSO was stirred under Ar at room temperature overnight. The reaction mixture was then treated with 3 mL acetonitrile and 80 mL diethyl ether. The resulting mixture was filtered to give the crude product, which was dried under vacuum and purified through crystallization in acetonitrile and diethyl ether. Yield: **2a:** 44 mg (67 %), **2b:** 50 mg (70 %).

Route 2 wth NaH: A mixture of **1a** (80.8 mg, 0.10 mmol) or **1b** (85.6 mg, 0.10 mmol) and NaH (60 % in mineral oil, 4.0 mg, 0.10 mmol) in 3 mL anhydrous DMF was stirred under Ar at -10 ^{o}C for 2 h and then at room temperature for 24 h. Excess diethyl ether was added and the resulting mixture was filtered. The crude product was dried under vacuum and purified through crystallization in acetonitrile and diethyl ether. Yield: **2a:** 32 mg (48 %), **2b:** 40 mg (56 %) .

Conversion from 2a/2b into 3a/3b. The solution of **2a** (66.2 mg, 0.10 mmol) or **2b** (71.0 mg, 0.10 mmol) in 5 mL DMSO was added dropwise into 100 mL saturated

NH_4PF_6 aqueous under stirring. The mixture was stirred under room temperature for 10 min and then filtered**.** The precipitate was washed with water and a little amount of methanol/diethyl ether (1:1) to give the crude product, which was dried under vacuum and purified through crystallization in acetonitrile and diethyl ether.

3a: orange solid. Yield: 73 mg, 90 %. ^{1}H NMR (400 MHz, CD_3CN): δ 10.43-10.16 (br, 1H), 8.45-8.27 (m, 2H), 8.22-8.02 (m, 2H), 7.82-7.74 (m, 1H), 7.73-7.58 (m, 3H), 7.57-7.18 (m, 6H), 6.60 (t, 1H), 4.85-4.72 (m, 1H), 4.71-4.56 (m, 1H), 4.51-4.36 (m, 2H), 4.20-4.85 (m, 4H). ^{13}C NMR (100MHz, DMSO-d^6): δ 180.37, 170.70, 155.72, 149.23, 146.73, 142.50, 139.44, 134.61, 134.15, 131.66, 126.71, 125.03, 124.26, 123.38, 122.74, 122.34, 116.45, 112.66, 111.21, 111.08, 107.92, 48.80, 46.10, 44.39, 44.04. Anal. Calcd for $C_{28}H_{25}N_7F_{12}P_2Ni$: C, 41.61; H, 3.12; N, 12.13. Found: C, 41.25; H, 3.50; N,11.95. ESI-MS (*m*/*z*): 516.42 $[M\text{-}H\text{-}2PF_6]^+$, 258.83 $[M\text{-}2PF_6]^{2+}$.

3b: red solid. Yield: 72 mg, 84%. ^{1}H NMR (400 MHz, CD_3CN): δ 10.90-10.0 (br, 1H), 8.63 (d, 1H), 8.40 (td, 1H), 8.36-8.30 (m, 1H), 8.24 (d, 1H), 7.84 (d, 1H), 7.75-7.65 (m, 2H), 7.64-7.52 (m, 3H), 7.50-7.25 (m, 5H), 6.55 (td, 1H), 4.88-4.78 (m, 1H), 4.62-4.47 (m, 3H), 4.30-4.21 (m, 1H), 4.17-3.98 (m, 3H). ^{13}C NMR (100MHz, CD_3CN): δ 181.17, 172.23, 152.66, 149.87, 144.77, 142.32, 136.58, 135.77, 129.99, 128.30, 128.11, 127.68, 127.12, 126.89, 124.49, 119.73, 114.39, 113.62, 113.42, 110.24, 51.92, 48.91, 48.11, 48.07. Anal. Calcd for $C_{28}H_{25}N_7F_{12}P_2Pd$: C, 39.29; H, 2.94; N,11.46. Found: C, 39.52; H, 3.12; N, 11.74. ESI-MS (*m*/*z*): 564.45 $[M\text{-}H\text{-}2PF_6]^+$, 282.85 $[M\text{-}2PF_6]^{2+}$.

Conversion from 3a/3b into 2a/2b. The solution of **3a** (80.8 mg, 0.10 mmol) or

3b (85.6 mg, 0.10 mmol) in 5mL DMSO was added dropwise into 100mL saturated Na_2CO_3 aqueous under stirring. The mixture was stirred under room temperature for 10 min and then filtered**.** The precipitate was washed with water and a little amount of methanol/diethyl ether (1:1) to give the crude product, which was dried under vacuum and purified through crystallization in acetonitrile and diethyl ether. Yield: **2a:** 69 mg (85%), **2b:** 66 mg (77 %).

Crystal Structure Determination.

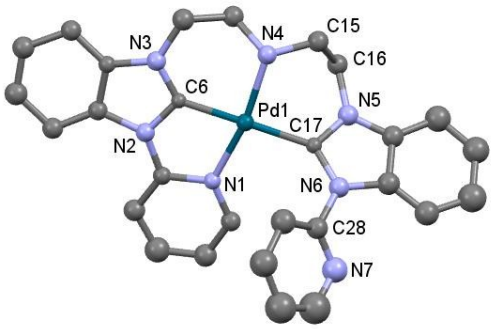
Single crystal X-ray diffraction data were collected for all structures on a Bruker APEX DUO diffractometer with a CCD area detector (Mo Kα radiation, λ= 0.71073 Å).[3] The APEX 2 program was used to obtain frames of data and determine lattice parameters. SAINT was used to integrate the data. The absorption corrections were applied using SADABS.[4] The structures were solved usingd SHELXS-97[5] and subsequently completed via Fourier recycling using SHELXL-2014 program.[6] All structures were solved using the direct method. Nonhydrogen atoms were refined by anisotropic displacement parameters. Crystallographic data, data collection, and refinement parameters for all complexes are listed in Tables S1-S2.

Table S1 Crystallographic data for **1a**·CH_3CN and **2a**.

	1a·CH_3CN	**2a**
CCDC	1839765	1839764
Formula	$C_{30}H_{28}F_{12}N_8NiP_2$	$C_{28}H_{24}F_6N_7NiP$
M	849.23	662.22
T/[K]	296(2)	296(2)
Crystal system	orthorhombic	monoclinic
Space group	$P\,2_12_12_1$	$P\,2_1/n$
a (Å)	11.1990(7)	8.3433(11)
b (Å)	15.1982(9)	28.320(4)
c (Å)	19.6380(14)	11.5936(17)
α (°)	90	90
β (°)	90	90.533(4)
γ (°)	90	90
V/[Å^3]	3342.5(4)	2739.2(7)
Z	4	4
D_{calc} (g cm^{-3})	1.688	1.606
μ (mm^{-1})	0.781	0.842
F (000)	2178	1352
θ rang (°)	2.259/27.549	2.270/25.999
Reflns collected	29210	19776
R_{int}	0.0415	0.1285
Indep. reflns	7682	5382
Refns obs. [I> 2σ(I)]	7141	4022
Data/restr./paras	7682/0/484	5382/0/388
GOF	1.031	1.013
R_1, wR_2 [all data]	0.0368/0.0758	0.0800/0.1293
R_1, wR_2 [I > 2σ(I)]	0.0328/0.0742	0.0550/0.1201
Larg.peak/hole (e. Å)	0.512/-0.408	1.012/-0.831

Table S2 Crystallographic data for **3a**·CH_3CN and **3b**·$2CH_3CN$.

	3a·CH_3CN	**3b**·$2CH_3CN$
CCDC	1839747	1839752
Formula	$C_{30}H_{28}F_{12}N_8NiP_2$	$C_{32}H_{31}F_{12}N_9P_2Pd$
M	849.23	938.00
T/[K]	296(2)	296(2)
Crystal system	monoclinic	monoclinic
Space group	$P\,2_1/c$	$P\,2_1/c$
a (Å)	10.7258(12)	14.6723(12)
b (Å)	18.871(2)	13.3927(12)
c (Å)	16.3402(17)	19.2473(15)
α (°)	90	90
β (°)	93.244(2)	108.953(2)
γ (°)	90	90
V/[Å^3]	3302.1(6)	3577.1(5)
Z	4	4
D_{calc} (g cm^{-3})	1.708	1.742
μ (mm^{-1})	0.791	0.711
F (000)	2178	1880
θ rang (°)	1.650/27.544	2.113/25.020
Reflns collected	28993	23460
R_{int}	0.0815	0.0457
Indep. reflns	7386	6298
Refns obs. [I> 2σ(I)]	4635	5527
Data/restr./paras	7386/12/483	6298/12/520
GOF	1.051	1.124
R_1, wR_2 [all data]	0.1105/0.1909	0.0496/0.1177
R_1, wR_2 [I > 2σ(I)]	0.0643/0.1639	0.0427/0.1135
Larg.peak/hole (e. Å)	1.528/-0.711	0.668/-0.722



Crystal system	monoclinic
Space group	*Cm*
a (Å)	19.068(6)
b (Å)	23.430(7)
c (Å)	8.321(2)
α (°)	90
β (°)	98.495(7)
γ (°)	90
V/[Å^3]	3676.8(19)
Z	2

Figure S1 Structure of **1b** and crystallographic data. Anions, solvent molecules, and all hydrogen atoms have been omitted for clarity. Thermal ellipsoids are set at 50% probability.

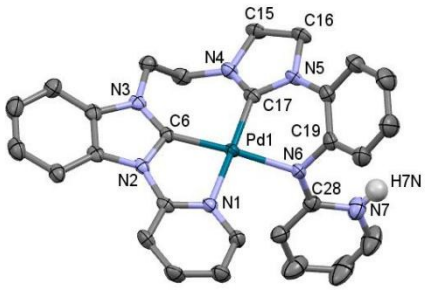
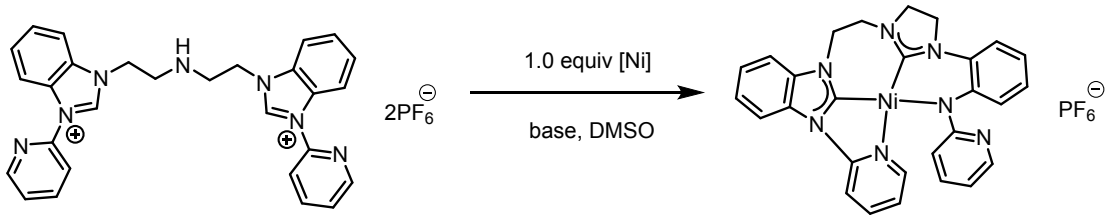


Figure S2 Molecular structure of **3b**·CH_3CN with ellipsoids set at 50 %. Solvent molecules and PF_6^- anions are removed for clarity. Only the pyridinium hydrogen atom is shown. Relevant bond lengths [Å] and angles [°] of **3b**: Pd1-N1 2.067(3), Pd1-C6 1.968(4), Pd1-C17 1.965(4), Pd1-N6 2.048(3), N6-C19 1.421(5), N6-C28 1.332(5), C17-Pd1-C6 99.15(16), C17-Pd1-N6 84.79(14), C6-Pd1-N1 79.56(14), N6-Pd1-N1 96.57(12).

Table S3 Summary of the reactions with some frequently used bases under different conditions.[a]



$(H_2L)(PF_6)_2$ **2a**

entry	[Ni]	base (equiv)	*T* (°C)	time (h)	yield (%)[b]
1[c]	$Ni(OAc)_2•4H_2O$	NEt_3	70	12	59
2	$Ni(OAc)_2•4H_2O$	Na_2CO_3 (3.0)	80	12	48
3	$Ni(OAc)_2•4H_2O$	$Na_2HPO_4•7H_2O$ (3.0)	80	12	44
4	$Ni(OAc)_2•4H_2O$	$K_3PO_4•3H_2O$ (3.0)	R. T.	24	56
5[d]	$Ni(OAc)_2•4H_2O$	NaOH (3.0)	R. T.	24	61
6[d]	$NiCl_2•6H_2O$	NaOH (3.0)	R. T.	24	55
7[e]	$NiCl_2$	NaH (3.3)	-10	24	32

[a]Reaction conditions: 0.10 mmol $(H_2L)(PF_6)_2$, 0.10 mmol $Ni(OAc)_2·4H_2O$, 3.0-7.0 equivalent of base in 3.0-5.0 mL DMSO for 12-24 h under Ar, followed by recrystallization of acetonitrile and diethyl ether. [b]Isolated yield after purification. [c]0.10 mL NEt_3 was added, a slightly lower temperature was set to avoid drastically refluxing of NEt_3. [d]5.0 mL DMSO was used. [e]3.0 mL anhydrous DMF was used. The reaction was stirred at -10 °C for 2 h before stirred for 24 h at room temperature.

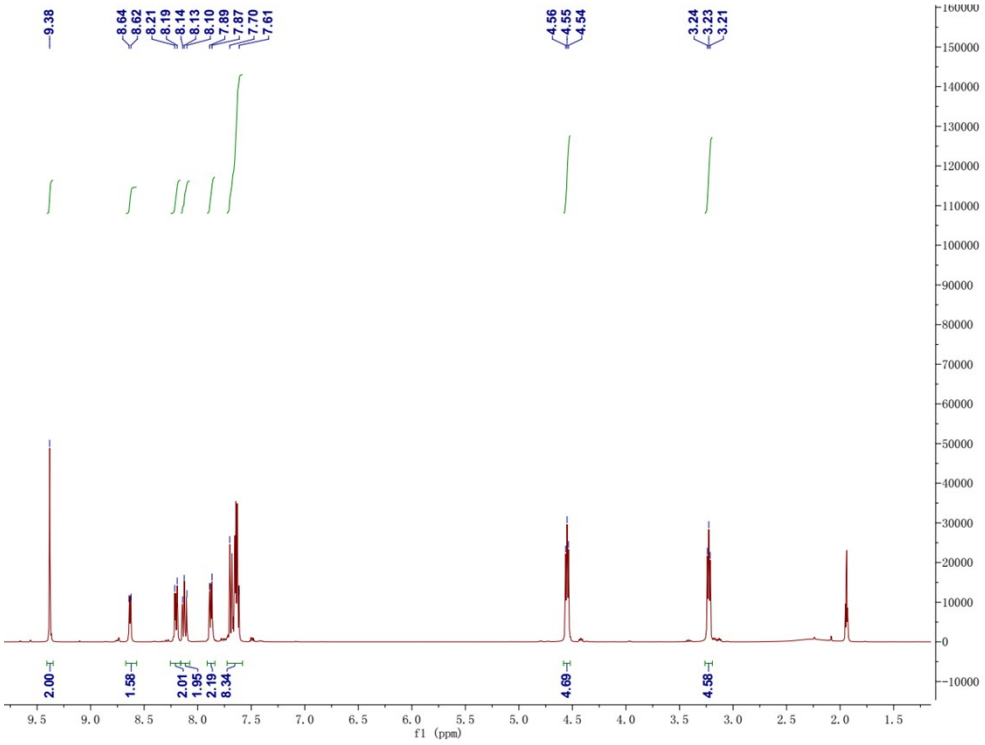


Figure S3 ^{1}H NMR spectrum of $(H_2L)(PF_6)_2$ in CD_3CN

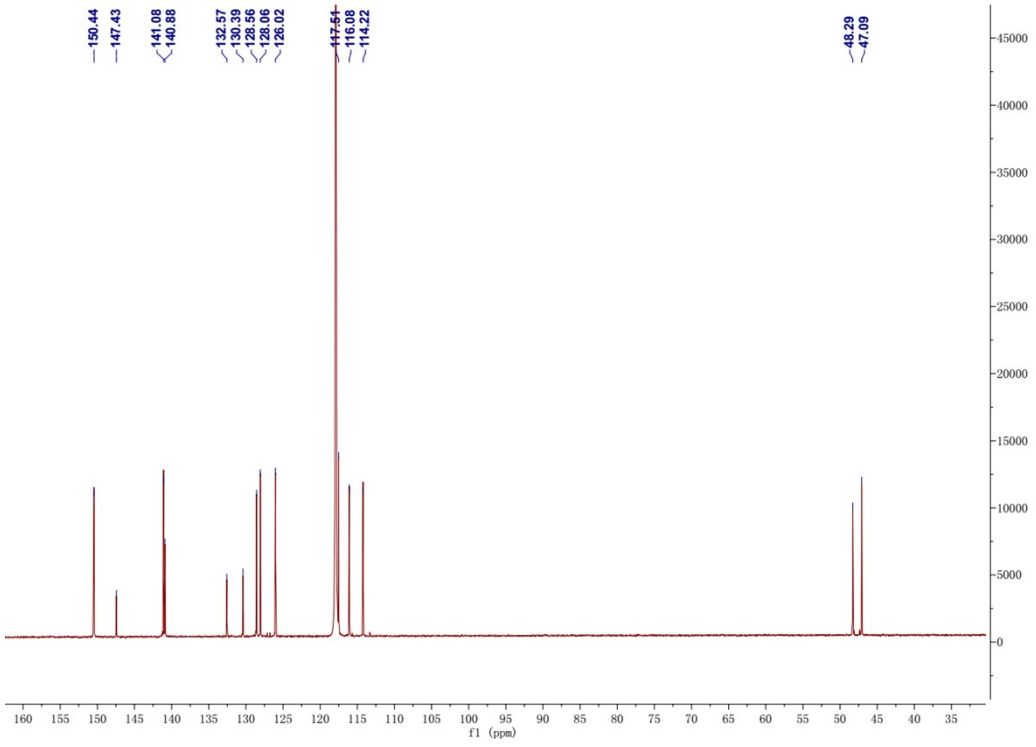


Figure S4 ^{13}C NMR spectrum of $(H_2L)(PF_6)_2$ in CD_3CN

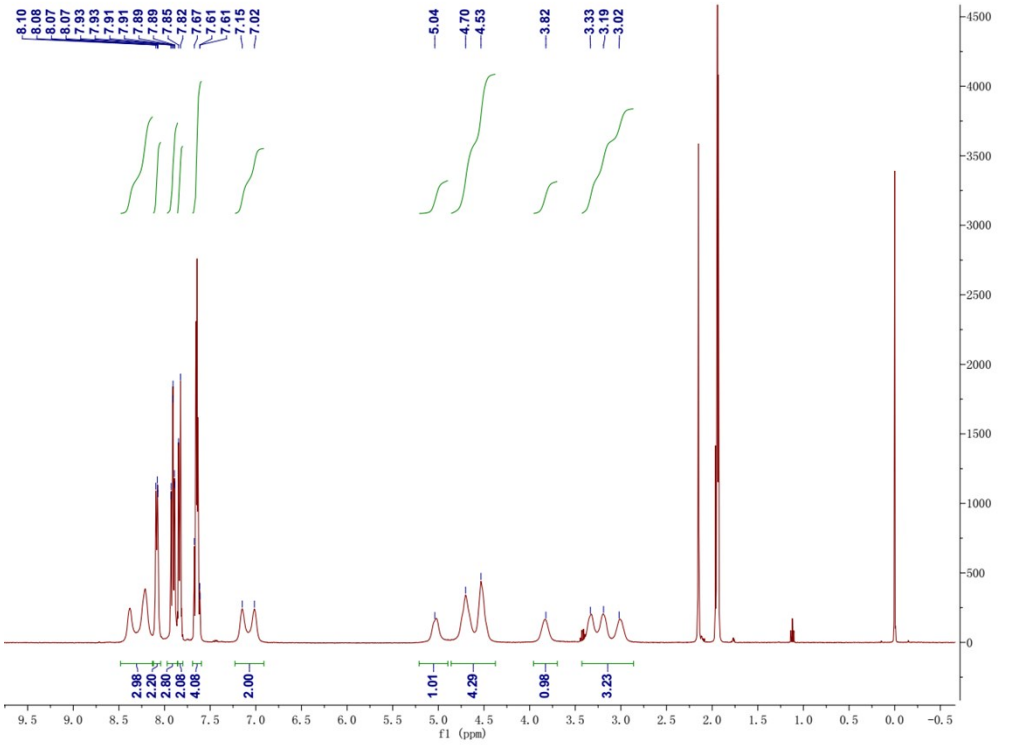


Figure S5 ^{1}H NMR spectrum of complex **1a** in CD_3CN

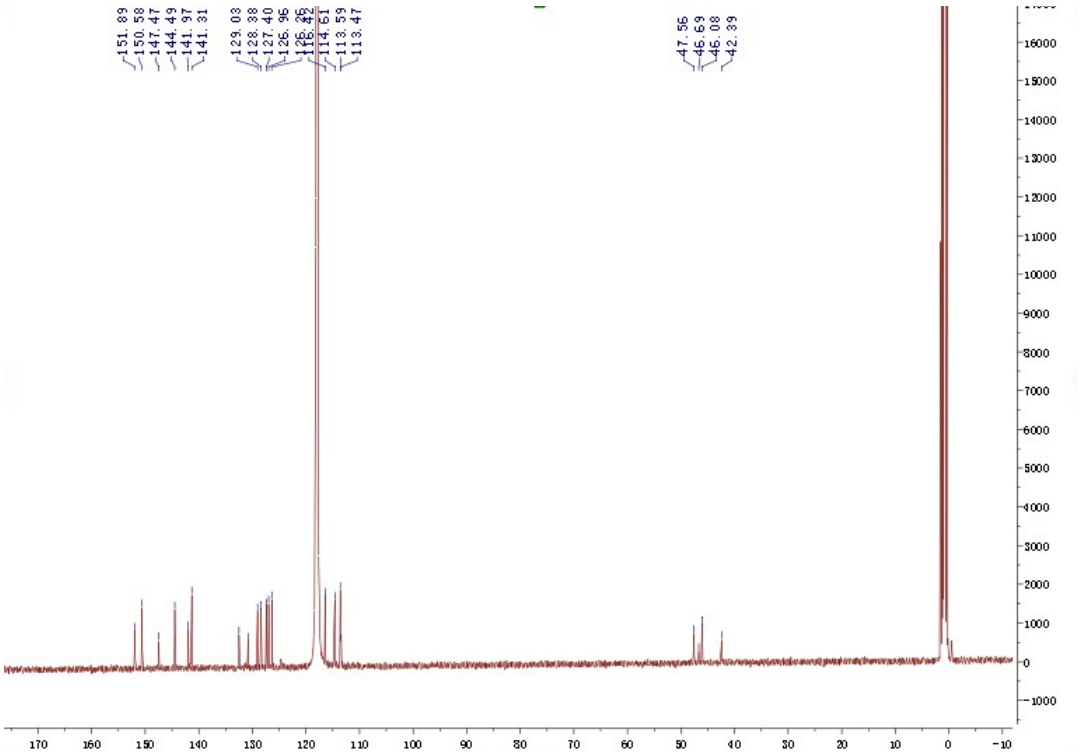


Figure S6 ^{13}C NMR spectrum of complex **1a** in CD_3CN

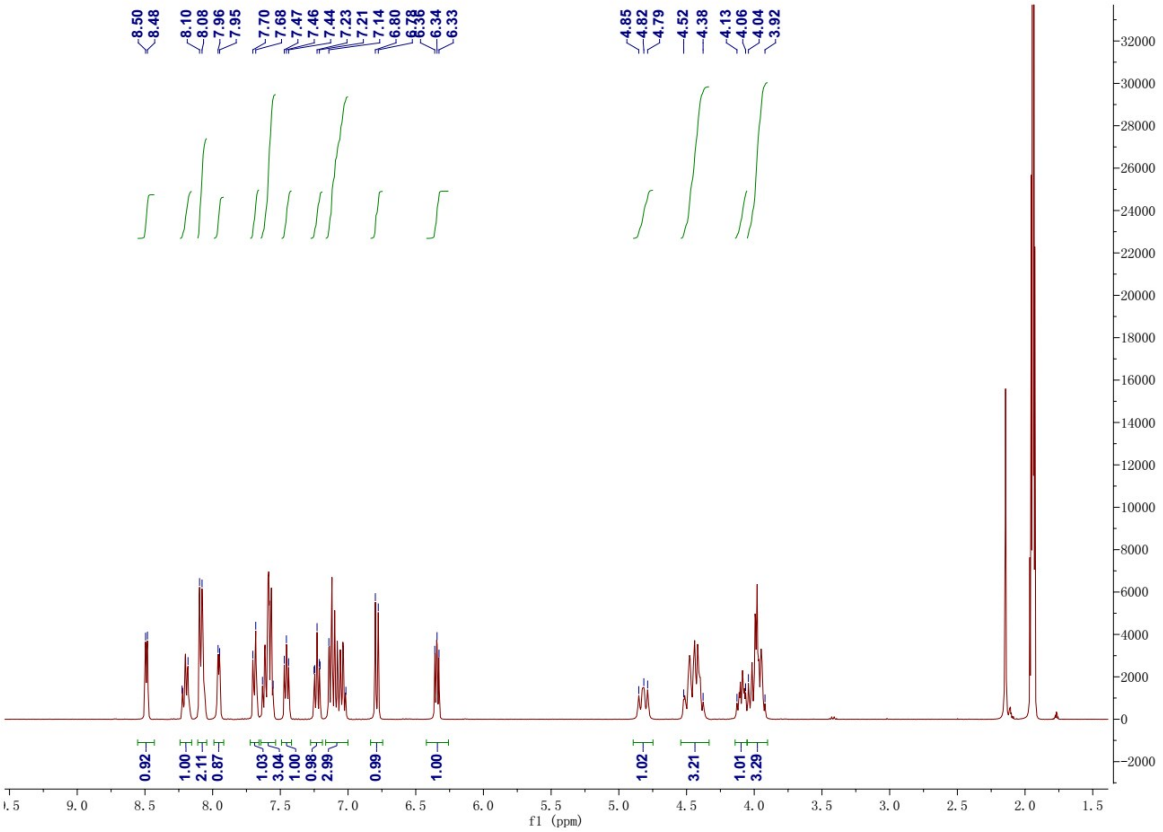


Figure S7 ^{1}H NMR spectrum of complex **2a** in CD_3CN

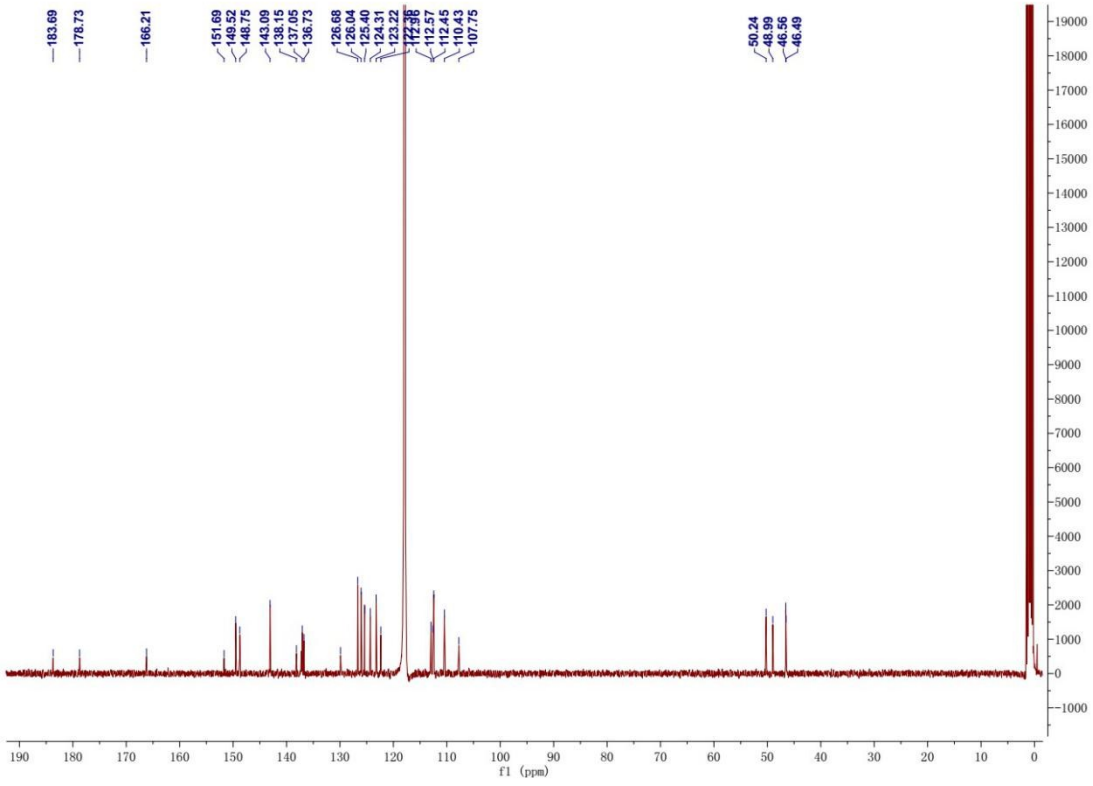


Figure S8 ^{13}C NMR spectrum of complex **2a** in CD_3CN

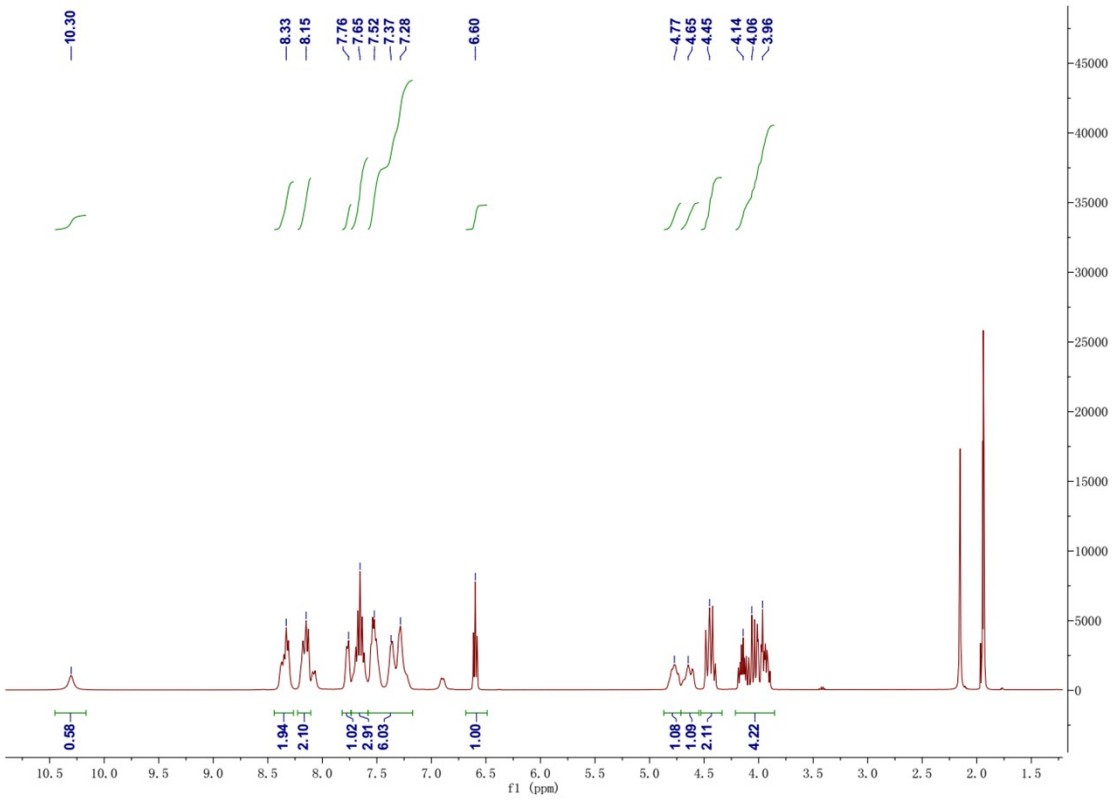


Figure S9 ^{1}H NMR spectrum of complex **3a** in CD_3CN

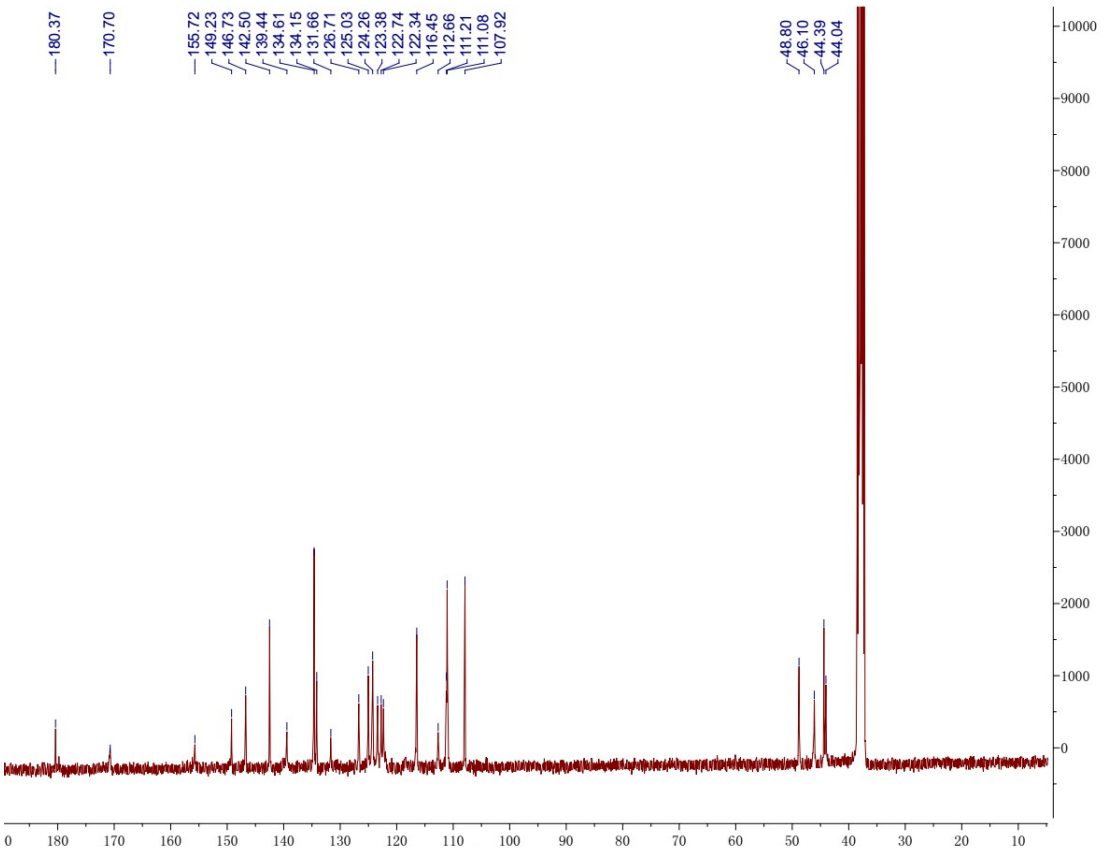


Figure S10 ^{13}C NMR spectrum of complex **3a** in d^6-DMSO

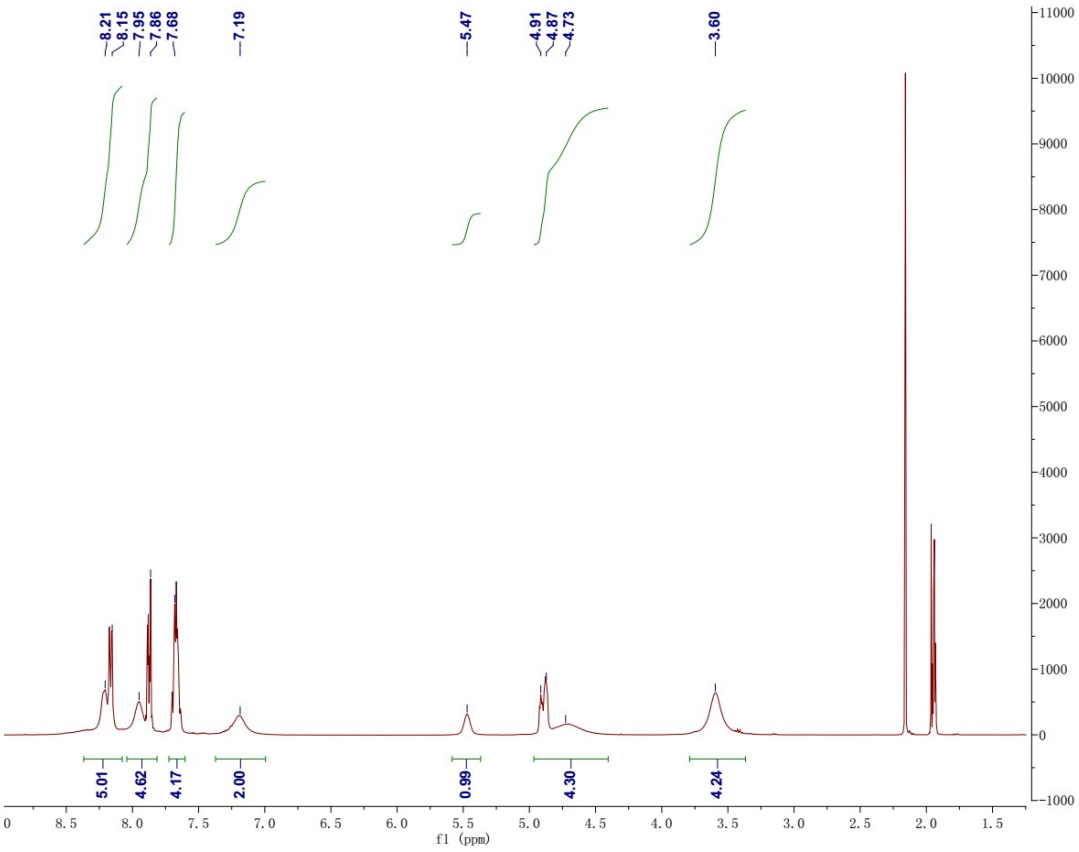


Figure S11 ^{1}H NMR spectrum of complex **1b** in CD_3CN

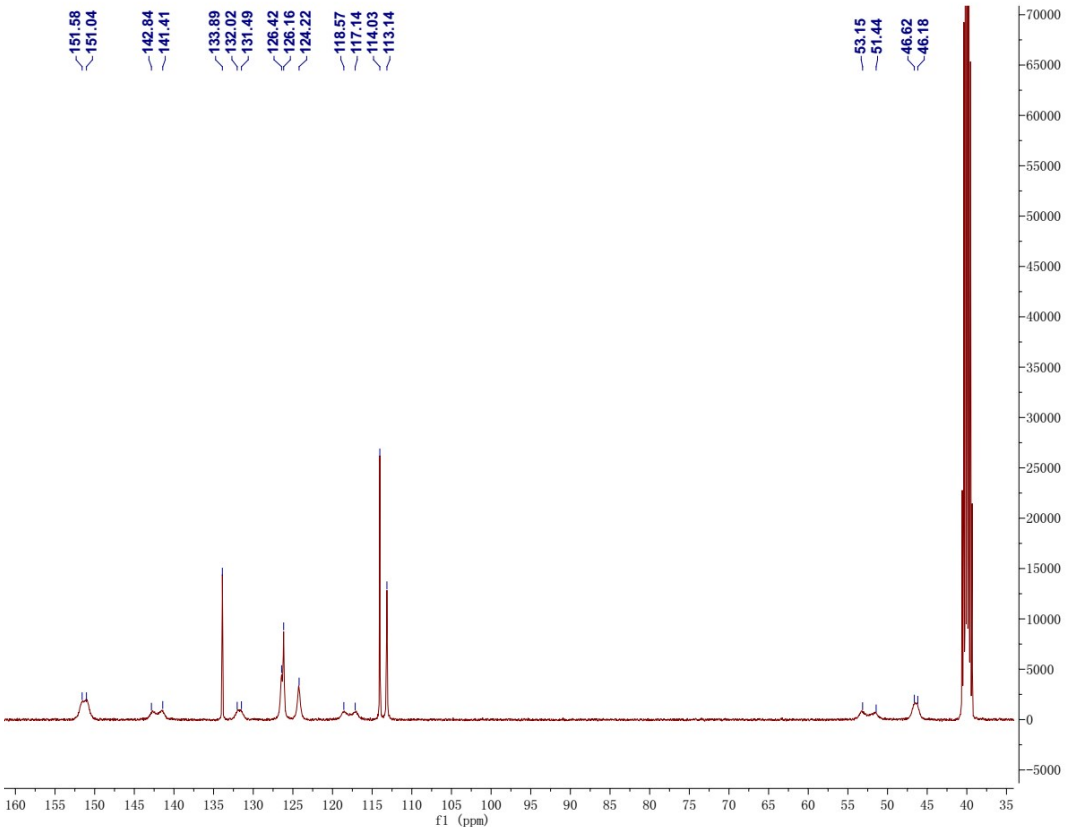


Figure S12 ^{13}C NMR spectrum of complex **1b** in d^6-DMSO

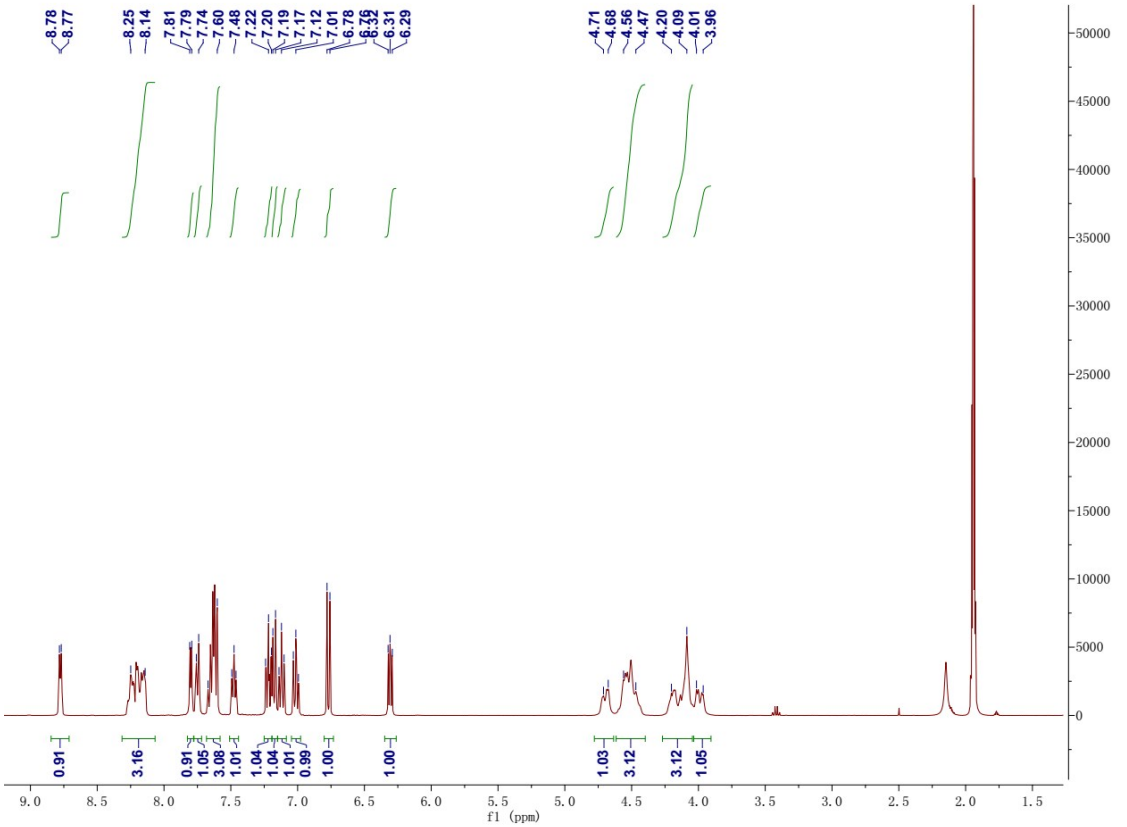


Figure S13 ^{1}H NMR spectrum of complex **2b** in CD_3CN

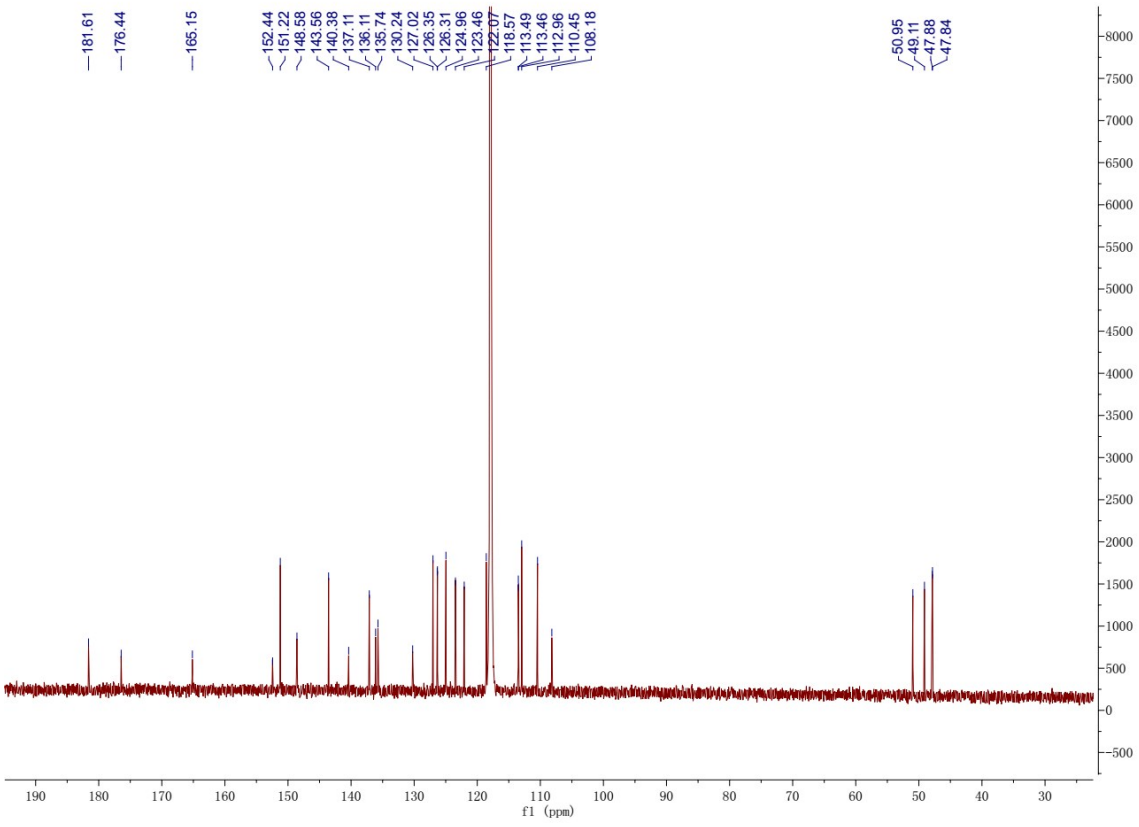


Figure S14 ^{13}C NMR spectrum of complex **2b** in CD_3CN

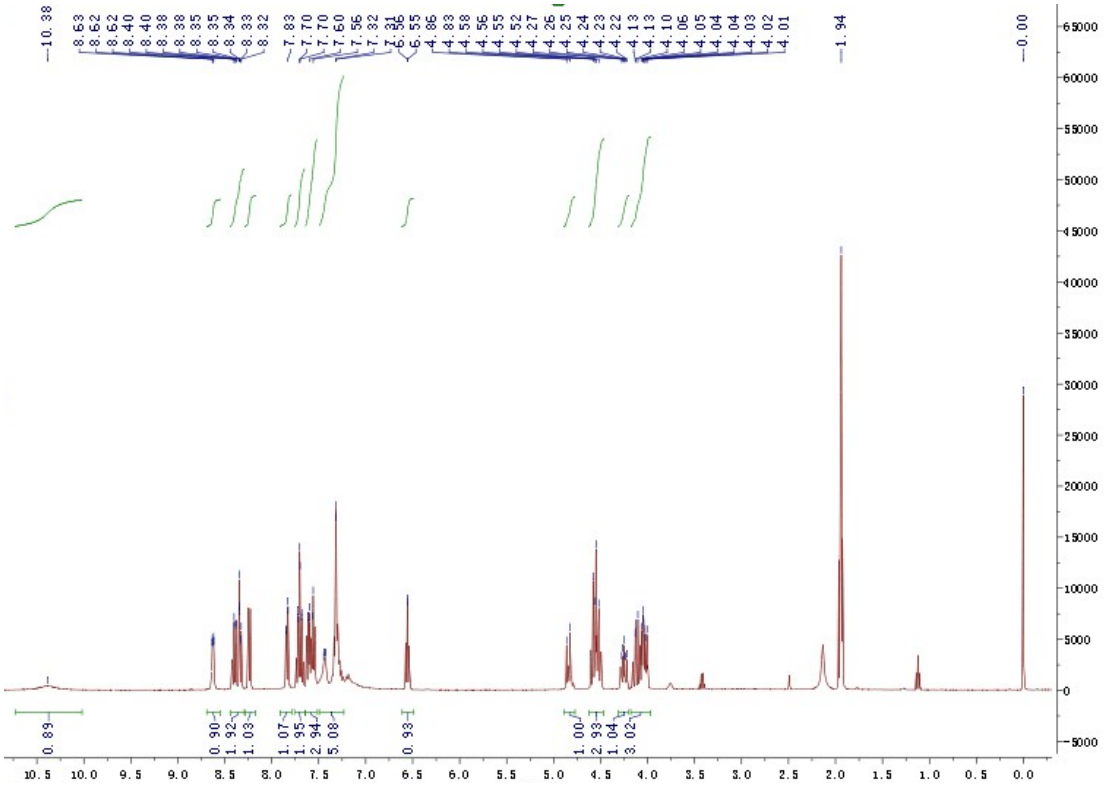


Figure S15 ^{1}H NMR spectrum of complex **3b** in CD_3CN

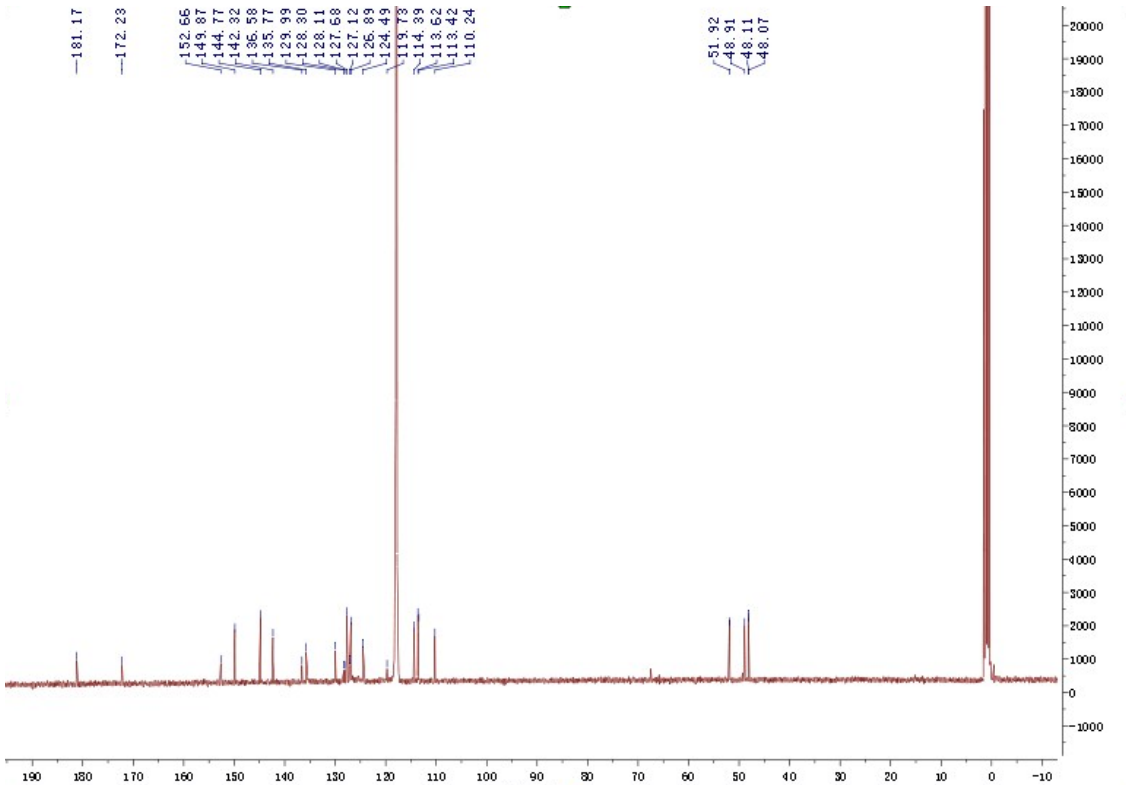


Figure S16 ^{13}C NMR spectrum of complex **3b** in CD_3CN

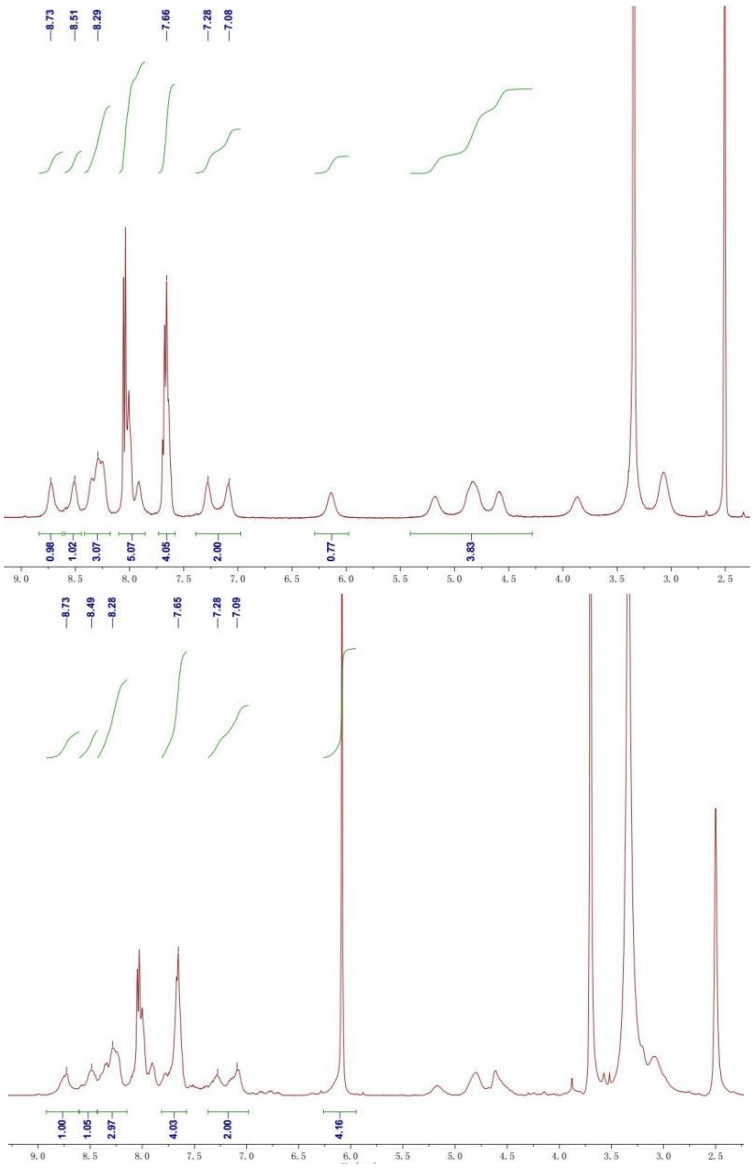


Figure S17 ^{1}H NMR spectrum of reaction mixture of 0.10 mmol $(H_2L)(PF_6)_2$ and 0.10 mmol $Ni(OAc)_2{\cdot}4H_2O$ in 3 mL d^6-DMSO for 24 h, in which 0.10 mmol 1,3,5-trimethoxybenzene was added as the internal standard (bottom). The ^{1}H NMR spectrum of **1a** is shown for comparision (top).

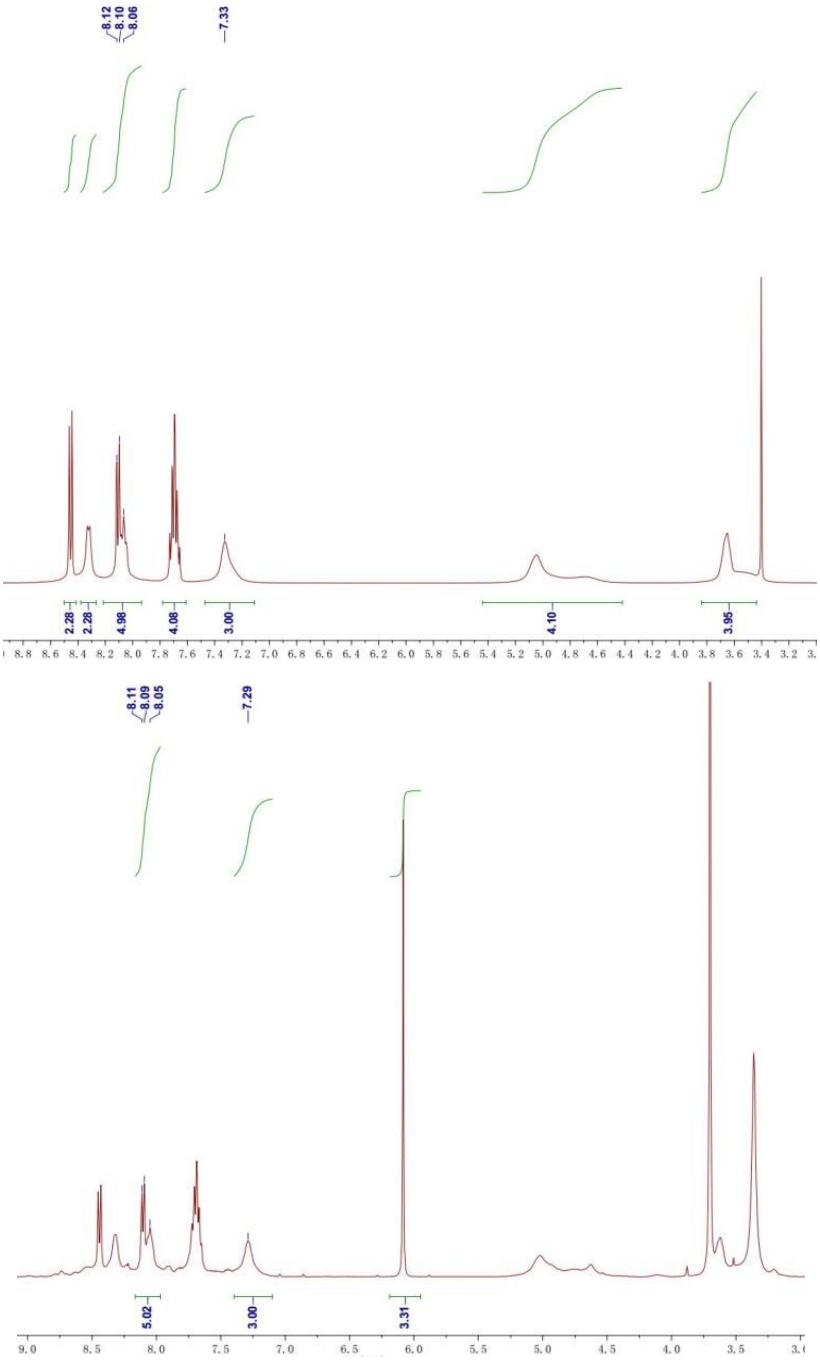


Figure S18 ^{1}H NMR spectrum of reaction mixture of 0.10 mmol $(H_2L)(PF_6)_2$ and 0.10 mmol $Pd(OAc)_2$ in 3 mL d^6-DMSO for 12 h, in which 0.10 mmol 1,3,5-trimethoxybenzene was added as the internal standard (bottom). The ^{1}H NMR spectrum of **1b** is shown for comparision (top).

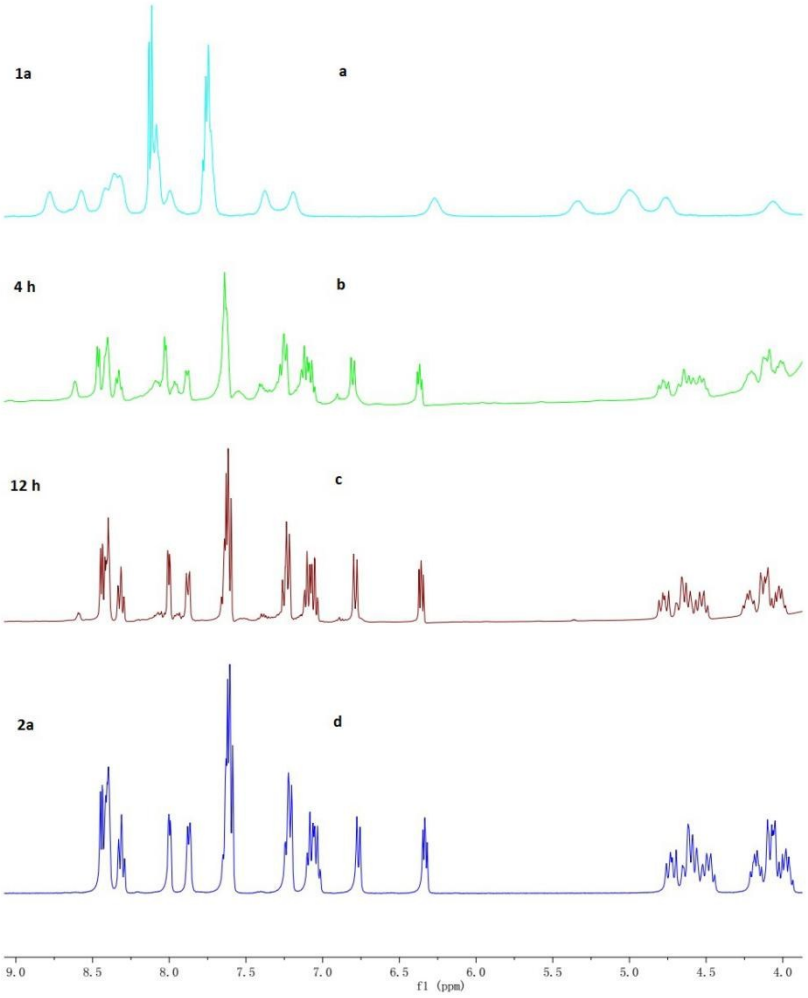


Figure S19 The ^{1}H NMR spectra of the reaction mixture of **1a** and 3 equiv of NaOAc in d^{6}-DMSO after reaction for 4 h (b) and 12 h (c). The spectra of **1a** (a) and **2a** (d) are shown for comparsion. It is clear that **1a** is cleanly converted into **2a** after 12 h.

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